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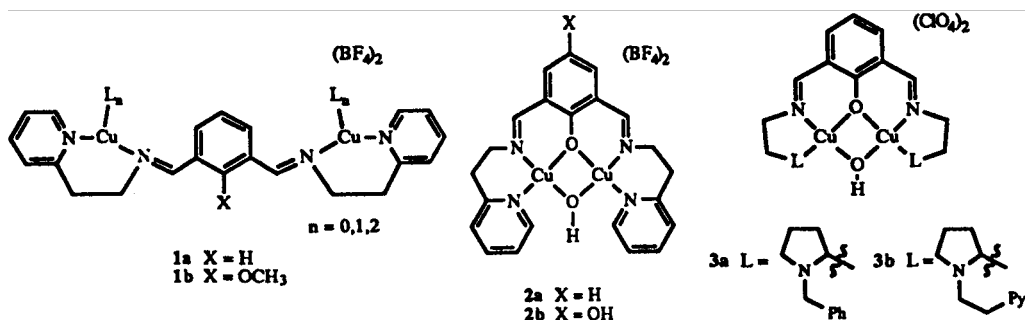
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L09 OXIDATION CATALYSIS: A DINUCLEAR APPROACH

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The binding and activation of molecular oxygen on polynuclear copper centers are essential features of various copper proteins such as the O₂-carrier hemocyanin and the monooxygenase tyrosinase. In biomimetic approach to new catalysts for stereoselective oxidations with O₂ achiral¹ and chiral non-racemic dinuclear copper(I) and copper(II) complexes **1-3** were prepared. The syntheses, molecular structures and reactivity in stoichiometric and catalytic oxidations with O₂ and oxygen-donors will be presented.



Arene hydroxylation, being a model system for monooxygenases, was observed for **1a** in the presence of O₂ whereas an intriguing hydroxylation-demethoxylation sequence was found for **1b**. A mechanistic study established dual oxidative pathways.

Using a pyridazine as a bridging unit between two Cu centers. O₂ activation is followed by hydroxylation α to the amine moiety in the ligand. We generated also hydroquinone Cu(II) complexes such as **2** and could demonstrate for the first time oxidative coupling and polymerisation reactions of phenols employing well-characterized dinuclear copper catalysts.

Modification of the chelating ligands in **2**, retaining the bridging 2,6-bisimino-phenol unit, resulted in novel dinuclear Cu(II) and Ni(II) complexes.³ Both complexes with four and five coordinated metal centers are presented. Structural and electrochemical properties as well as results on catalytic epoxidations with various oxygen donors will be reported.

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